p - **BLOCK ELEMENTS**

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p-BLOCK ,Group - 15

>The Group 15 elements are: (Elements with atomic number) Nitrogen (N) \rightarrow 7(non metal) Phosphorus (P) \rightarrow 15(non metal) Arsenic (As) \rightarrow 33(metalloid) Antimony (Sb) \rightarrow 51(metalloid) Bismuth (Bi) \rightarrow 83(metal)

>Configuration: N \rightarrow 1s² 2s² 2p³ (ns² np³)

The s-orbital in these elements is completely filled and p-orbital is half filled making their electronic configuration extra stable.



Size:

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As we move from top to bottom, there's an increase in the size because of the increase in the number of shells. From N to P, there's an increase in the size but from As to Bi, only a small increase in the size because of the presence of completely filled d- and/or f-orbital in higher members(increased nuclear charge due to poor screening effect).

Ionization Enthalpy:

Since the size and screening effect increases down the group, ionization enthalpy decreases down the group.

Electronegativity:

since the size increases, tendency to attract the shared pair of electron will decrease and hence electronegativity will decrease.

- Metallic properties-Metallic character increases down
- Density-Increases down the group

Physical Properties:

- All the elements of this group are polyatomic.
- Dinitrogen (N_2) is a diatomic gas while all others are solid.
- Nitrogen and Phosphorus are non-metals, Arsenic and Antimony are metalloids and Bismuth is a metal.
- Except Nitrogen, all other elements show allotropic nature. Chemical properties:

Oxidation states:

- They show oxidation state of -3, +3 and +5.
- Tendency to exist -3 oxidation state decreases down the group due to increase in size and metallic character.
- Bismuth hardly shows -3 oxidation state.
- The stability of +5 oxidation state decreases down the group and that of +3 oxidation state increases. This is because of inert pair effect.
- The only well established +5 oxidation state in Bismuth is in <u>BiF5.</u>
- Nitrogen shows all oxidation states from -3 to +5

Anomalous nature of nitrogen: Nitrogen differs from the rest of the members of this group due to its smaller size , high electronegativity , high ionization enthalpy and non – availability of d orbitals.

♦ Nitrogen has unique ability to form p П- pП multiple bonds with itself and with other elements
♦ Nitrogen is a gas other elements are solids.
♦ Nitrogen cannot extend the valency more than 4. Maximum covalency of nitrogen is 4.

Reactivity towards Hydrogen

- Group 15 elements form hydrides of the formula EH₃ where E is the element of group 15.
- Hydrides show regular gradation in their properties i.e.
- Thermal stability decreases from NH₃ to BiH₃ because of decrease in bond dissociation enthalpy. NH₃ > PH₃ > AsH₃ > SbH₃ > BiH₃
- Reducing character of hydrides increases i.e. NH₃ (ammonia) is the strongest reducing agent while BiH₃ is the weakest.

NH₃ <PH₃<AsH₃ <SbH₃< BiH₃

- □ Bond angle decreases in the order NH₃ > PH₃ > AsH₃ > SbH₃ > BiH₃
- PH₃ has lower boiling point than NH₃. PH₃ molecules are not associated through hydrogen bonding in liquid state.

 $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$

Reactivity towards Oxygen

- ▶ They form two types of oxides E_2O_3 and E_2O_5 .
- > The oxide in higher oxidation state (E_2O_5) is more acidic.

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- Acidic character decreases down the group.
- Oxides of the type E₂O₃ of Nitrogen and Phosphorus are purely acidic, of Arsenic and Antimony are amphoteric and of Bismuth are Basic.

Reactivity towards Halogen

- ▶ They form halides of the formula EX₃ and EX₅.
- Nitrogen does not form penta halide due to non-availability of the dorbitals in the valence shell.
- Penta halides are more covalent than tri halides.
- All the tri halides except Nitrogen are stable. NF₃ is the most stable tri halide of Nitrogen.
- ► Tri halides except BiF₃ are covalent in nature.

Reactivity towards Metals

These elements react with metals to form their binary compounds exhibiting -3 oxidation state.

Examples:

Ca₃N₂ (Calcium Nitride) Ca₃P₂ (Calcium Phosphide) Na₃As₂ (Sodium Arsenide)



Preparation:

a) Lab preparation

 $NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(l) + NaCl (aq)$

b) General-Thermal decomposition of ammonium dichromate

 $(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3$

c) Thermal Decomposition of Na or Ba azide

 $Ba(N_3)_2 \rightarrow Ba + 3N_2$



Properties

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- ► It has two stable isotopes: ¹⁴N and ¹⁵N.
- It has a very low solubility in water.
- It is quite inert at room temperature because of high bond enthalpy of N≡N bond.
- As temperature increases, reactivity increases

It shows the following reactions:

 $\begin{array}{l} 6\text{Li} + \text{N}_2 \rightarrow 2\text{Li}_3\text{N} \\ 3\text{Mg} + \text{N}_2 \rightarrow \text{Mg}_3\text{N}_2 \\ \text{N}_2 \ (\text{g}) + 3\text{H}_2 \ (\text{g}) \rightarrow 2\text{NH}_3 \ (\text{g}) \ [\text{Haber's process}] \end{array}$

AMMONIA

Preparation

Decay of nitrogenous organic compounds.

 $NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightarrow 2NH_3 + H_2O + CO_2$

On small scale

 $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$ $(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$

On large scale-Haber's process

 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

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conditions :~Pressure of about 200 atm.

~Temperature of about 700 K.

~Catalyst- Iron oxide with small amounts of $K_2O_{}$ and Al_2O_3

flow chart for the production of NH₃ by Haber's process.



Properties

1. Structure of Ammonia:

It has pyramidal structure with one lone pair of electrons. Hybridization present is sp³ but the tetrahedral angle gets reduced to 107.8° because of repulsion of lone pair of electrons.



- 2. Ammonia gas is highly soluble in water and its aqueous solution is weakly basic due to the formation of OH- ions. NH₃ (g) + H₂O (l) \rightarrow NH₄⁺ (aq) + OH⁻ (aq)
- 3. In water, Ammonia forms hydroxide which is knows as Ammonium Hydroxide.

Ammonia precipitates metal ions as hydroxides ZnSO₄ (aq)+ 2NH₄OH (aq) \rightarrow Zn(OH)₂ (s) + (NH₄)₂SO₄ (aq) (White ppt)

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\begin{array}{l} \mbox{2FeCl}_3 \mbox{ (aq) + NH_4OH (aq) } \rightarrow \mbox{Fe}_2 O_3.xH_2O + NH_4Cl \mbox{ (aq)} \\ \mbox{ (Brown ppt)} \end{array}
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Metal ions like Cu^{2+} and Ag^+ detected using Ammonia a) Cu^{2+} (aq) + 4NH₃ (aq) \rightarrow [Cu (NH₃)₄]²⁺(aq) (Blue) (Deep blue)

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b) Ag^+ (aq) + Cl^- (aq) \rightarrow AgCl (s)
(Colourless) (White ppt)
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NITRIC ACID

Preparation of Nitric Acid

1. Lab preparation

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NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3
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2. On a large scale it is prepared mainly by Ostwald's process.

(a) NH_3 is oxidized by atmospheric oxygen in presence of Pt/Rh catalyst at 500K and 9 bar pressure

 $4NH_3$ (g) + $5O_2$ (g) $\rightarrow 4NO$ (g) + $6H_2O$ (g)

(b)NO is further oxidized to NO₂

 $2NO+O_2 \rightarrow 2NO_2$

(c)NO₂ dissolves in water and HNO₃ is formed 3NO₂ (g) + H₂O (l) \rightarrow 2HNO₃ (aq) + NO (g)

Structure of Nitric acid:



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Properties

- 1. In the gaseous state, it exists as a planar molecule.
- 2. It behaves as a strong acid giving hydronium and nitrate ions. HNO₃(aq) + H₂O(l) \rightarrow H₃O⁺(aq) + NO₃⁻(aq)
- 3. Concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum.

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 $3Cu + 8 HNO_3(dilute) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$ $Cu + 4HNO_3(conc.) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$ $4Zn + 10HNO_3(dilute) \rightarrow 4 Zn (NO_3)_2 + 5H_2O + N_2O$ $Zn + 4HNO_3(conc.) \rightarrow Zn (NO_3)_2 + 2H_2O + 2NO_2$

- 4. Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a film of oxide on the surface.
- 5. Concentrated nitric acid also oxidizes non-metals
 - $I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10 NO_2 + 4H_2O$
 - $C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2$
 - $S_8 + 48HNO_3(conc.) \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O_3$
 - $P_4 + 20HNO_3(conc.) \rightarrow 4H_3PO_4 + 20 NO_2 + 4H_2O_3$

Brown ring test of Nitrates

To a Nitrate sample solution, freshly prepared Ferrous Sulphate solution is added and then conc. H_2SO_4 acid along the side of the test tube is added, then a brown ring at the interphase is formed.

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NO_3 + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O
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$$\label{eq:Fe} \begin{split} \mbox{[Fe $(H_2O)_6$]^{2+}$} + NO & \rightarrow \mbox{[Fe $(H_2O)_5$ $(NO)]^{2+}$} + \mbox{H}_2O \\ & (Brown) \end{split}$$

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GROUP 16

includes:

- 1. Oxygen (O)-8(non metal)
- 2. Sulphur (S)-16(non metal)
- 3. Selenium (Se)-34(metalloid)
- 4. Tellurium (Te)- 52(metalloid)
- 5. Polonium (Po)- 84 (Metal)

□ Electronic Configuration :

The elements of group 16 have six electrons in the outermost shell and have ns²np⁴ general electronic configuration

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Atomic and Ionic Radii

□ Ionisation Enthalpy :

Ionisation enthalpy decrease down the group. It is due to increase in size. However, the element of this group have lower ionisation enthalpy values compared to those of group 15 in the corresponding periods

Electron Gain Enthalpy :

Because of the compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However from sulphur onwards the value again becomes less negative upto polonium.

□ Electronegativity :

Next to fluorine, oxygen has the highest electronegativity value amongst the elements. Within the group, electronegativity decrease with an increase in atomic number. This implies that the metallic character

increase from oxygen to polonium.



Chemical Properties :

- Oxidation states and trends in chemical reactivity :
- The elements of group 16 exhibit a number of oxidation states.
- The stability of -2 oxidation state decreases down the group.
- Polonium hardly shows -2 oxidation states.
- Since electronegativity of oxygen is very high, it shows only negative oxidation states as -2 except in the case of OF_2 where its oxidation states is + 2.
- Other elements of the group exhibit + 2 + 4 + 6 oxidation states but + 4 and + 6 are more common.
- Sulphur, selenium and tellurium usually show + 4 oxidation in their compounds with oxygen and +6 oxidations state with fluorine.
- The stability of +6 oxidation state decreases down the group and stability of +4 oxidation state increases (inert pair effect).

Reactivity towards Hydrogen

- \blacktriangleright All the elements combine with hydrogen to form hydrides of the type $H_2 E$
- Acidic character increases from top to bottom because of decrease in bond dissociation enthalpy down the group
- Thermal stability decreases down the group because of the increase in the bond length
- Except water all hydrides have reducing property and this increases down the group.

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Reactivity towards Hydrogen

Hydride/Property	B	ond length	gth Bond		Thermal		Acidic		Reducing	
			enthalpy		stability		property		property	
H2O		Increases		Decreases		Decreases		Increases		Increases
H2S		down the		down the		down the		down the		down the
H2Se		group		group		group		group		group
H2Te	1	,	١	,		,	,	•		,

Reactivity towards Oxygen

► All the elements form oxides of the formula EO₂ and EO₃

- Reducing properties of dioxides decreases down the group
- All oxides are acidic in nature .

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Reactivity towards Halogens

- > They form a large number of halides of the formula EX_6 , EX_4 , EX_2
- The stability of the halides decreases down the group, in the order F > Cl > Br > 1 (Stability decreasing)
- Among Hexahalides, Hexa fluorides are the only stable halides. They are gaseous in nature and have octahedral structure.
- All elements except selenium form dichlorides and dibromides. These dihalides are formed by sp3 hybridisation and thus have tetrahedral structure.
- Amongst terrafluorides, SF4 is a gas, SeF4 liquid and TeF4 a solid. These fluorides have sp³d hybridisation
- > Sulphur hexafluoride, SF_6 is exceptionally stable for steric reasons.

DIOXYGEN (o₂)

Preparation of Dioxygen

1. From KClO₃

$$2\text{KClO}_3 \xrightarrow{\text{Heat}}{\text{MnO}_2} \rightarrow 2\text{KCl} + 3\text{O}_2$$

2. From Oxides (Thermal decomposition of oxides of metals)

3. From decomposition of hydrogen peroxide

 $2H_2O_2(aq) \rightarrow 2H_2O(1) + O_2(g)$

4. On a large scale it is prepared by electrolysis of water

Properties of O₂

- Dioxygen is odourless and colourless
- It is paramagnetic inspite of having 'even' number of electrons
- It reacts with nearly all metals and non-metals except gold, platinum and some noble gases.

Some of the common reactions of Dioxygen are

 $2\mathrm{Ca} + \mathrm{O}_2 \rightarrow 2\mathrm{CaO}$ $4Al + 3O_2 \rightarrow 2Al_2O_3$ $P_4 + 5O_2 \rightarrow P_4O_{10}$ $C + O_2 \rightarrow CO_2$ $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$ $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_2$

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Oxides are a binary compound of oxygen with another element.
Oxides can be simple (MgO, Al₂O₃) or mixed (Pb₃O₄, Fe₃O₄)
Another way of classification of simple oxides isa) Acidic
Basic

- c) Amphoteric and
- d) Neutral

ACIDIC OXIDE

~An oxide which combines with water to give an acid is called an Acidic Oxide E.g.. : SO₂, CO₂, N₂O₅

~Generally non-metallic oxides are acidic

BASIC OXIDE

The oxides which give a base on reaction with water are called Basic Oxides E.g.. : Na₂O, CaO, BaO
Generally, metallic oxides are basic in nature

AMPHOTERIC OXIDE

~These are oxides which exhibit a dual behavior i.e. they show properties of both acidic and basic oxides E.g.. : Al₂O₃

$$\begin{aligned} Al_{2}O_{3}(s) + 6HCl(aq) + 9H_{2}O(1) \rightarrow 2[Al(H_{2}O)_{6}]^{3+}(aq) + 6Cl^{-}(aq) \\ Al_{2}O_{3}(s) + 6NaOH(aq) + 3H_{2}O(1) \rightarrow 2Na_{3}[Al(OH)_{6}](aq) \end{aligned}$$

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NEUTRAL OXIDE

~Oxides which are neither acidic nor basic E.g.. : CO, NO, N₂O

OZONE

- Ozone is an allotropic forms of oxygen
- ▶ It is formed from atmospheric oxygen in the presence of sunlight
- Ozone protects the earth's surface from excessive concentration of ultraviolet (UV) radiations
- ▶ It is a pale blue gas, dark blue liquid or violet-black solid
 - It is prepared by passing silent electric discharge through pure and dry oxygen

$$3O_2 \rightleftharpoons 2O_3$$

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Ozone is thermodynamically unstable and gives dioxygen and nascent oxygen on decomposition and because of this nascent oxygen, it is a powerful oxidising agent Two chemical reactions to show the oxidising nature of ozone are

$$\begin{split} \text{PbS(s)} &+ 4\text{O}_3(g) \rightarrow \text{PbSO}_4(s) + 4\text{O}_2(g) \\ 2\text{I}^-(\text{aq}) &+ \text{H}_2\text{O}(l) + \text{O}_3(g) \rightarrow 2\text{OH}^-(\text{aq}) + \text{I}_2(s) + \text{O}_2(g) \end{split}$$

When ozone reacts with an excess of potassium iodide solution , iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O_3 gas.

The structure of ozone is as follows

Ozone saves us from the UV radiations but there is a depletion in the ozone concentration in the upper layer of the atmosphere due to supersonic jet airoplanes and use of freons which are used in the aerosol sprays and as refrigerants.

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SULPHUR

- Sulphur exists in numerous allotropes of which two are the most important which are yellow rhombic (α) and monoclinic (β)
- > At room temperature, Rhombic is stabler and it transforms to monoclinic sulphur when heated above 369 K
- Rhombic Sulphur is
 - ~yellow in colour
 - ~melting point 385.8 K
 - \sim specific gravity 2.06
 - ~formed on evaporating the solution of Roll Sulphur in carbon disulphide
- ~insoluble in water and readily soluble in carbon disulphide
- Monoclinic sulphur
 ~melting point 393 K
 ~specific gravity 1.98
 ~soluble in carbon disulphide
 ~prepared by melting rhombic sulphur in a dish and cooling

- BLOCK Yellow Rhombic Sulphur C Sulphur 37

- α sulphur is stable below 369 K and transforms into β sulphur above this temperature. At 369 K both the forms are stable, hence this temperature is called – Transition Temperature
- Both Rhombic and Monoclinic Sulphur have S₈ molecules. They both have puckered or typical forms. Several other modifications of sulphur containing 6 – 20 atoms per ring have been prepared.

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In vapour state sulphur partly exists as S₂ molecule which has two unpaired electrons in the antibonding π * orbitals like O₂ and, hence, exhibits paramagnetism.

SULPHUR DIOXIDE

Methods of Preparation:

- General Method $S(s) + O_2 \rightarrow SO_2(g)$
- ► Lab Method $SO_3^{2-}(aq) + 2H^+ \rightarrow H_2O(1) + SO_2(g)$
- Industrial Method

 $4\text{FeS}_{2}(g) + 11\text{O}_{2}(g) \rightarrow 2\text{Fe}_{2}\text{O}_{3}(s) + 8\text{SO}_{2}(g)$

Properties:

- Colourless gas,Pungent smell,Highly soluble in water
- When passed through water forms sulphurous acid (H_2SO_3)
- When passed through NaOH

 $2NaOH + SO_2 \rightarrow Na_2SO_3$, $Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$

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Properties continued....

- When made to react with chlorine it gives sulphuryl chloride SO₂ (g) + Cl₂ (g) \rightarrow SO₂Cl₂ (l)
- When reacted with oxygen in presence of vanadium (V) pentoxide forms sulphur dioxide $2SO_2(g) + O_2(g) \xrightarrow{v_{2OS}} 2SO_3(g)$

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- It behaves as Reducing agents
- Converts $Fe^{3+} \rightarrow Fe^{2+}$ $2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$
- ► Decolourises acidified KMnO4 solution $5SO_2 + 2MnO_4^- + 2H2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$
- ► It is used for detection of SO₂
- Its angular in shape, Resonating structures:

Group 17

includes:

- 1. Fluorine (F)
- 2. Chlorine (Cl)
- 3. Bromine (Br)
- 4. lodine (I)
- 5. Astatine (At) (Radioactive)

Electronic Configuration :

All these elements have seven electrons in their outermost shell (ns2 np5) which is one electron short of the next noble gas.

Atomic and Ionic Radii :

The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge . Atomic and ionic radii increase from fluorine to iodine due to increasing number of quantum shells.

Ionisation Enthalpy :

They have little tendency to lose electron. Thus they have very high ionisation enthalpy. Due to increase in atomic size, ionisation enthalpy dereases down the group.

Electron Gain Enthalpy :

Halogen have maximum negative electrons gain enthalpy in the corresponding period. The negative electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small 2p orbitals of fluorine and thus, the incoming electron does not experience much attraction.

Electronegativity :They have very high electronegativity. The electronegativity decreases down the group. Fluorine is the most electronegativeelement in the periodic table

- Halogens are coloured F_2 , has yellow, Cl_2 , greenish yellow, Br_2 , red and I_2 , violet colour.
- $^\circ$ One curious anomaly $% 10^\circ$ is the smaller enthalpy of dissociation of F_2 compared to that of Cl_2

Chemical Properties Oxidation states and trends in chemical reactivity All the halogens exhibit -1 oxidation state. However, chlorine, bromine and iodine exhibit +1, +3, +5 and +7oxidation states also. The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms e.g., in interhalogens, oxides and oxoacids. The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only -1 oxidation state.

 F_2 is the strongest oxidizing halogen and it oxidises other halide ions in solution or even in the solid phase. The decreasing oxidising ability of the halogen in aqueous solution down the group is evident from their standard electrode potentials.

> $2F_{2}(g) + 2H_{2}O(\ell) \rightarrow 4H^{+}(aq) + 4F^{-}(aq) + O_{2}(g)$ $X_{2}(g) + H_{2}O(\ell) \rightarrow HX(aq) + HOX(aq)$ (where X = Cl or Br)

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Reactivity of Hydrogen towards Halogens.

- 1. They form Hydrogen Halides. $H_2+X_2 \rightarrow 2HX$
- 2. Stability of Halides decreases down the group. HF is most stable.
- 3. Acid strength increases down the group. HF is most reactive.
- 4. Acid strength \rightarrow HF < HCl < HBr < HI

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Reactivity of oxygen towards halogens:

- 1. When oxygen combines with halogens, it forms oxides except when oxygen and Fluorine combine together the compound formed called oxygen fluoride..
- Fluorine and oxygen forms two compounds OF₂ and O₂F₂. OF₂ is thermally stable. → Both of them are good fluorinating agents
- 3. Chlorine forms oxide with the formula Cl₂O, ClO₂, Cl₂O₆, Cl₂O₇. ClO₂ is a very good bleaching agent for paper pulp and textile and in water treatment.
- 4. Bromine oxides are the least stable halogen oxides which exist only at low temp. They are powerful oxidizing agents. Common formulae for Bromine oxides are Br₂O, BrO₂, BrO₃.
- 5. Iodine oxides are insoluble solids and decompose on heating. Their oxides have the formula I_2O_4 , I_2O_3 and I_2O_7 . I_2O_5 is a strong oxidising agent and is used in the estimation of carbon monoxide.

Reactivity of Halogens towards metals.

Halogen and metals form Metal Halides. For example, Magnesium with Bromide form Magnesium Bromide.

 $Mg + Br_2 \rightarrow MgBr_2$

- Ionic character decreases down the group. That means MF is more ionic.
 MF> MCl > MBr > MI
- If a metal exhibits more than one oxidation state than the halide in higher oxidation state is more covalent i.e. SnCl₄, PbCl₄, and SbCl₄ are more covalent than SnCl₂, PbCl₂ and SbCl₃.

CHLORINE

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Methods for the preparation of Chlorine.

- $\blacktriangleright MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$
- $\bullet 4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$
- $\blacktriangleright 2KMnO_4 + 16 HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

Deacon's process

- When HCl gas is treated with atmospheric oxygen in presence of $CuCl_2$ as catalyst at 723K we get chlorine gas.
- $\bullet \quad 4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$

Electrolytic Process

It is prepared by electrolysis of Brine i.e. concentrated NaCl solution. Chlorine is obtained at anode.

Properties of chlorine

- Greenish yellow gas with pungent and suffocating smell
- Soluble in water
- Heavier in air
- It reacts with metals and non-metals to form chlorides $2Al + 3Cl_2 \rightarrow 2AlCl_3$
 - $2Na + Cl_2 \rightarrow 2NaCl$
 - $2Fe + 3Cl_2 \rightarrow 2FeCl_2$
 - $P_4 + 6Cl_2 \rightarrow 4PCl_3$
 - $S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$
- It has high affinity for hydrogen. Therefore, it combines with compounds containing hydrogen and hydrogen itself to give HCl. $H_2 + Cl_2 \rightarrow 2HCl$

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• Reaction with H_2

 $\begin{array}{c} H_2 + Cl_2 \rightarrow 2HCl \\ H_2S + Cl_2 \rightarrow 2HCl + S \\ C_{10}H_{16} + 8Cl_2 \rightarrow 16HCl + 10C \end{array}$

- Reaction of ammonia with chlorine $8NH_3 + 3Cl_2 \rightarrow 6NH_4Cl + N_2$ (excess) $NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$ (excess)
- ► Reaction of ammonia with alkalies 2NaOH (cold, dilute) + Cl₂ → NaCl + NaOCl + H₂O 6NaOH (hot, conc) + 3Cl₂ → 5NaCl + NaClO₃ + 3H₂O
- ► Reaction with dry slaked lime 2Ca(OH) 2 + 2Cl2 → Ca(OCl) 2 + CaCl2 + 2H2O

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Chlorine water on long standing it looses its yellow colour due to the formation of HCl and HOCl. This HOCl gives nascent oxygen which is responsible for oxidizing and bleaching properties of chlorine.

```
Cl2 + H2O ---- \rightarrow HCl + HOCl
```

HOCl \longrightarrow HCl + (O)

Q. Give equation showing the oxidation properties of chlorine.

```
Ans. 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{Cl}_2 \rightarrow \text{Fe}_2 (\text{SO}_4)_3 + 2\text{HCl}
```

```
Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl
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```
SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl
```

Chlorine water bleaches vegetable or organic matter in presence of moisture. It has permanent bleaching effect.

HYDROGEN CHLORIDE

Preparation in Lab :

- $\blacktriangleright \text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$
- ► NaHSO₄ + NaCl \rightarrow Na₂SO₄ + HCl

Properties :

- 1. Colourless gas with pungent smell
- 2. Extremely soluble in water

HCl (g) + H₂O (l) \rightarrow H₃O⁺ (aq) + Cl⁻ (aq)

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- 3. In aqueous solution it is called Hydrochloric acid.
- 4. It reacts with ammonia $NH_3 + HCl \rightarrow NH_4Cl$
- 5. It reacts with ammonia to give ammonium chloride (dense white fumes)
- 6. When three parts of concentrated HCl are mixed with one part of concentrated HNO_3 we get aqua regia. This is used in dissolving noble metals.

 $Au + 4H^+ + NO^{3-} + 4Cl^- \rightarrow AuCl^{4-} + NO + 2H_2O$

 $3Pt + 16 H^+ + 4NO^{3-} + 18Cl^- \rightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$

7.Hydrochloric acid decomposes salts of weaker acids $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$ $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$ $Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$ Oxoacids of Halogens

Due to high electronegativity and small size, chlorine forms only one oxoacid HOF.

Halic (I) acid	HOF	HOCl	HOBr	HOI
(Hypohalous acid)	(Hypofluorous acid)	(Hypochlorous acid)	(Hypobromous acid)	(Hypoiodous acid)
Halic (III) acid	-	HOCIO	-	-
(Halous acid)	-	(chlorous acid)	-	-
Halic (V) acid	-	HOCIO ₂	HOBrO ₂	HOIO ₂
(Halic acid)		(chloric acid)	(bromic acid)	(iodic acid)
Halic (VII) acid	-	HOCIO ₃	HOBrO ₃	HOIO ₃
(Perhalic acid)		(perchloric acid)	(perbromic acid)	(periodic acid)

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Interhalogen compounds

When one Halogen combines with other Halogen atom the compound formed is known as Interhalogen compounds can have the following formula XX', XX'₃, XX'₅ and XX'₇ where X is the larger halogen than X

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Туре	Formula	Physical state and colour	Structure
XX'1	C1F	colourless gas	-
	BrF	pale brown gas	-
	IF^{a}	detected spectroscopically	-
	BrC1 ^b	gas	
	IC1	ruby red solid (α-form)	-
		brown red solid (β-form)	-
	IBr	black solid	-
XX'3	$C1F_3$	colourless gas	Bent T-shaped
	BrF_3	yellow green liquid	Bent T-shaped
	IF ₃	yellow powder	Bent T-shaped (?)
	ICl ₃ ^c	orange solid	Bent T-shaped (?)
XX'5	IF_5	colourless gas but	Square
		solid below 77 K	pyramidal
	BrF_5	colourless liquid	Square
			pyramidal
	$C1F_5$	colourless liquid	Square
			pyramidal
XX'7	IF ₇	colourless gas	Pentagonal
		—	bipyramidal

 a Very unstable; b The pure solid is known at room temperature; c Dimerises as Cl–bridged dimer (I_2Cl_6)

Internalogen compounds

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- Most of the portion already covered.
- Interhalogen compounds are prepared by direct combination of the two halogens. The product formed depends upon the conditions given:

 $\begin{array}{ll} \mathrm{Cl}_2 + \mathrm{F}_2 & \xrightarrow{437\,\mathrm{K}} 2\mathrm{ClF}; & \mathrm{I}_2 + 3\mathrm{Cl}_2 \rightarrow 2\mathrm{ICl}_3 \\ (\mathrm{equal \,volume}) & & \mathrm{I}_2 + 3\mathrm{F}_2 \rightarrow 2\mathrm{ICl}_3 \\ \mathrm{Cl}_2 + 3\mathrm{F}_2 & \xrightarrow{573\,\mathrm{K}} 2\mathrm{ClF}_3; & & \mathrm{Br}_2 + 3\mathrm{F}_2 \rightarrow 2\mathrm{BrF}_3 \\ (\mathrm{excess}) & & & (\mathrm{diluted\,with\,water}) \\ \mathrm{I}_2 + \mathrm{Cl}_2 \rightarrow 2\mathrm{ICl}; & & & \mathrm{Br}_2 + 5\mathrm{F}_2 \rightarrow 2\mathrm{BrF}_5 \\ (\mathrm{equimolar}) & & & \mathrm{Br}_2 + 5\mathrm{F}_2 \rightarrow 2\mathrm{BrF}_5 \end{array}$

As the ratio between radii of X and X' increases, the number of atoms per molecule also increases.

• Their physical properties are intermediate which means that the of constituent's halogens except their melting point and boiling point are little higher than expected.

Interhalogen compounds

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- Interhalogen compounds are more reactive than halogen except Fluorine because X-X' bond in interhalogens is weaker than X-X bond in halogens except F-F' bond.
- All of them undergo hydrolysis
- $\blacktriangleright XX' + H_2O \rightarrow HX' + HOX$
- ► Their structure can be explained VSEPR Theory.
- $\blacktriangleright XX_3 \text{ has bent 'T' shape.}$
- $\blacktriangleright XX_5 \rightarrow square pyramidal$
- $\blacktriangleright IX_7 \rightarrow pentagonal bipyramidal$

GROUP 18

- ► Helium (He)
- Neon (Ne)
- Argon (Ar)
- Krypton (Kr)
- Xenon (Xe)
- Radon (Rn)

- 1. All noble gases except radon occur in nature.
- 2. Radon is obtained as a decay product of Radium

$$^{226}_{88}$$
Ra $\rightarrow ~^{222}_{86}$ Rn $+^4_2$ He

- 3. The general configuration is ns²np⁶ and are noble gases because they generally do not interact with most of the elements.
- 4. Due to stable configuration, they have very high ionization enthalpy.
- 5. They are monotonic, colorless and sparingly soluble in water.
- 6. They have low melting and boiling points because of only type of inter-atomic interaction in these elements is weak dispersion forces.
- 7. Helium has lowest boiling point of 4.2K and has an unusual property of diffusing through most commonly used gas materials like rubber, glass or plastics.

- ✤ Neil Bartlett, prepared a red compound which is formulated as O₂+PtF₆⁺. He, then realised that the first ionisation enthalpy of molecular oxygen (1175 kJmol−1) was almost identical with that of xenon (1170 kJ mol−1). He made efforts to prepare same type of compound with Xe and was successful in preparing another red colour compound Xe⁺PtF₆⁻ by mixing PtF6 and xenon.
- Xenon forms three fluorides under three specific conditions

* Another method of preparation of XeF_6 is

 $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

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They are powerful fluorinating agents and are readily hydrolysed by water.

 $2XeF_2$ (s) + $2H_2O(l) \rightarrow 2Xe$ (g) + 4 HF(aq) + $O_2(g)$

- There structures are deduced from VSEPR theory
 - XeF_2 linear
 - XeF₄ square planar
 - XeF₆ distorted octahedral
- Xenon fluorides react with fluorides to form cationic species and fluoro anions.

 $\operatorname{XeF}_2 + \operatorname{PF}_5 \to [\operatorname{XeF}]^+ [\operatorname{PF}_6]^-$; $\operatorname{XeF}_4 + \operatorname{SbF}_5 \to [\operatorname{XeF}_3]^+ [\operatorname{SbF}_6]^ \operatorname{XeF}_6 + \operatorname{MF} \to \operatorname{M}^+ [\operatorname{XeF}_7]^-$ (M = Na, K, Rb or Cs)

Hydrolysis of XeF₄ and XeF₆

1. The hydrolysis is shown as follows $6XeF_4 + 12 H_2O \rightarrow 4Xe + 2XeO_3 + 24 HF + 3 O_2$ $XeF_6 + 3 H_2O \rightarrow XeO_3 + 6 HF$

2. Partial hydrolysis of XeF₆ gives the following $XeF_6 + H_2O \rightarrow XeOF_4 + 2$ HF $XeF_6 + 2$ $H_2O \rightarrow XeO_2F_2 + 4HF$

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- 3. XeO_3 is a colorless explosive solid with pyramidal structure
- 4. XeF₄ is a colorless volatile liquid with square pyramidal structure

